Relation of the Composition to the Properties of Clays

By

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Abstract

Most clays are composed essentially of minute particles of one or more of the clay minerals of which the kaolinite, montmorillonite, and illite groups are most important. The clay minerals occur in flake-shaped particles, possess base-exchange capacity, and exist in or are reducible to extremely small grain sizes on working with water. Different clay minerals possess these properties in varying degrees.

The clay mineral component is the chief factor determining the properties of a clay. In general, plasticity and bond strength caused by the clay minerals decrease in the following order: montmorillonite, illite, and kaolinite. In many clays, the plasticity and bond strength mainly result from the presence of the montmorillonite minerals or some members of the illite group, although these constituents may compose only minor amounts of the clay. The influence of the clay minerals on other properties is considered.

The green properties of clays are also related to the character of the exchangeable bases carried by the clay minerals. The fundamental reasons for the differences in properties resulting from different mineral constituents and various exchangeable bases are considered. The properties of clays are related further to the effective size-grade distribution developed in actual use which frequently differs from the size-grade obtained by mechanical analyses.

I. Introduction

The concept that most clays are essentially aggregates of very minute particles of one or more of a few minerals, known as the clay minerals, has been well established in recent years. Because the clay minerals are crystalline, it follows that clays are composed of material which is crystalline rather than amorphous. In addition to the clay minerals, some clays also contain, usually in minor amounts, such constituents as quartz, limonite (ferric-iron hydroxide), and organic material. The so-called colloid content of a clay is the percentage of these constituents, particularly the clay minerals, which it contains in particles smaller than a certain size.

Researches in a few laboratories have lately yielded much information on the structure and certain properties of the clay minerals. It is proposed here to consider this information and to attempt to derive therefrom a picture of the make-up of clays which will provide a satisfactory understanding of such properties as plasticity, green strength, and shrinkage. It is proposed also to analyze the influence of specific clay minerals and specific exchangeable bases on certain properties of clay. Other factors, not considered herein because they are of minor importance for most clays, also exert an influence on the properties of clay.

II. Clay Minerals

Mineralogical analyses of a large number of clays have shown that there are three important groups of clay minerals. Clays, therefore, generally are composed of a member or members of the three groups.

(1) Kaolinite

The chief member of this group is the mineral, kaolinite, with the composition $(OH)_8Al_4Si_4O_{10}$. Dickite and nacrite with similar compositions but different crystallographic forms are rare in sediments. Another member, anauxite, which differs from kaolinite by having a higher silicon and a lower aluminum content, is not a common mineral.

(2) Montmorillonite

This group takes its name from the mineral, montmorillonite, with the composition $(OH)_4Al_4Si_8O_{20} \cdot x \, H_2O$. Although not normally written in the formula, montmorillonite usually contains magnesium. Beidellite, reported to have a lower silicon and higher aluminum content, and nontronite, in which the aluminum has been replaced by ferric iron, are usually placed in this group. Recent work has suggested that saponite can be classed as a montmorillonite in which the aluminum has been replaced completely by magnesium.

(3) Illite

This group includes the abundant and widely distributed clay minerals which are similar but not identical with muscovite. So-called "hydromica" and "sericite-like" material belong in this group. The general formula of members of the group may be written $(OH)_4K_y(Al_4 \cdot Fe_4 \cdot Mg_4 \cdot Mg_6)$ $(Si_{8-y} \cdot Al_y)O_{20}$. When y equals 2 and magnesium and iron are not present, this is the formula for muscovite. In all illites which have been studied, only a small amount of iron replaces the aluminum, and y is considerably less than 2, varying from about 1 to 1.5. After future work has indicated the range of variation of composition within the illite group, it may be desirable to give specific names to members.

Other clay minerals, such as halloysite, are known,

but they will not be considered in the present paper because, in general, they are not important constituents of clays.
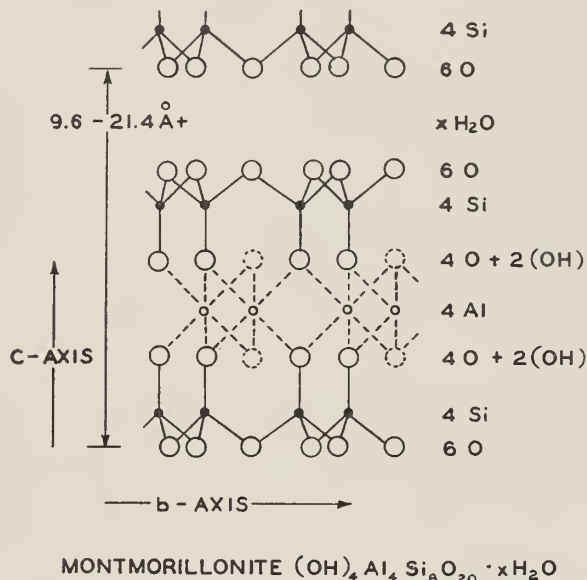

$$9.6 - 21.4 \overset{\circ}{A}+$$

MONTMORILLONITE $(OH)_4 Al_4 Si_8 O_{20} \cdot x H_2O$

Fig. 1.—Schematic presentation of crystal structure of montmorillonite (modified after Hofmann, *et al.*, *Z. Krist.*, **86** [5–6] 340–48 (1933)).

III. Properties of Clay Minerals

Only those properties of clay minerals that affect the physical properties of clays will be considered in the following discussion.

(1) Lattice Structure

The general structural features of the clay minerals have been well established by work in several laboratories following generalizations made by Pauling[1] in 1930. Two units are involved in these structures. One is the alumina or aluminum hydroxide unit which consists of two sheets of closely packed oxygens or hydroxyls between which aluminum atoms are embedded in such a position that they are equidistant from six oxygens or hydroxyls. Actually only two-thirds of the possible aluminum positions are occupied in this unit, which is the gibbsite structure. The mineral, brucite, possesses a similar structure except that all possible aluminum positions are occupied by magnesium. The second unit consists of a sheet of tetrahedral silica (SiO_4) groups linked to form a hexagonal network of the composition Si_4O_{10} when repeated indefinitely. This unit may be viewed as a sheet of loosely packed oxygen atoms with each oxygen linked to two silicon atoms directly beneath. The silicon atoms are in tetrahedral positions, three valencies being satisfied by linkage to three oxygens in the overlying sheet. The fourth silicon valency is satisfied below by an O atom such that silicon valency is analogous to the common (OH) group of gibbsite.

[1] See reference 103 in Bibliography, p. 151.

Montmorillonite consists of structural units of one gibbsite sheet between two sheets of tetrahedral silica groups (Fig. 1) stacked one above another in the direction of the *c*-axis. The structural units are loosely held together with water present between them. The *c* dimension varies with the H_2O content, and the mineral is said to have an expanding lattice. Analytical data suggest that the Al^{+++} of the gibbsite layer may be replaced by Fe^{+++} or Mg^{++}, in the former case yielding nontronite. The beidellite member of the montmorillonite group, reported to have a lower silica-to-alumina molecular ratio, might suggest the possibility of a small amount of replacement of Si^{++++} by Al^{+++} in the silica tetrahedral sheets. The implications of the unbalanced character of the lattice resulting from some of these replacements will be discussed presently.

ILLITE $(OH)_4 K_y (Al_4 \cdot Fe_4 \cdot Mg_4 \cdot Mg_6)(Si_{8-y} \cdot Al_y) O_{20}$
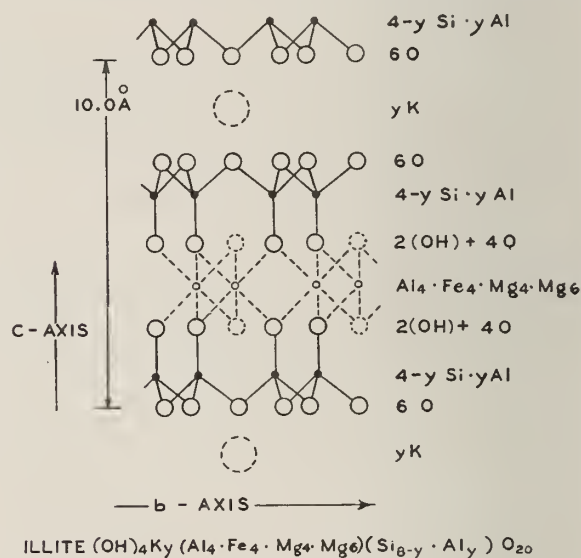
Fig. 2.—Schematic presentation of crystal structure of illite.

The structure of illite (Fig. 2) is similar to that of montmorillonite. It also consists of units of one gibbsite sheet between two sheets of tetrahedral silica groups. In the illite structure, however, considerable Al^{+++} replaces Si^{++++}, and the excess charge is balanced chiefly by K^+. The same situation prevails in muscovite in which one fourth of the Si^{++++} is replaced by Al^{+++}, with K^+ balancing the excess charge. In illite, there is less than one fourth of the Si^{++++} replaced by Al^{+++}. The *c* dimension of the illite unit cell does not change with varying water content. Illites, which have been studied to date, indicate that some magnesium and iron may replace aluminum in the gibbsite layer. Both illite and montmorillonite may carry some Mg^{++} in the possible Al^{+++} positions not occupied in gibbsite, *i.e.*, in brucite positions. Ca^{++} probably does not replace Al^{+++} because the atom is too large to fit.

The kaolinite structure (Fig. 3) is composed of units of one gibbsite sheet with a single sheet of tetrahedral silica groups. The lattice structure does not expand

with varying water content, and no replacements by iron or magnesium of the aluminum in the gibbsite layer have been proved. To account for variations in the silica-to-alumina ratio of members of this group of clay minerals, it was first suggested that Al^{+++} could be replaced by Si^{++++}. A recent, more favored explanation is that some of the Al^{+++} positions are vacant with correlary changes of O and OH to balance the charges in the lattice.

(2) Particle Shape

Montmorillonite, illite, and kaolinite have pronounced basal cleavage, which takes place with relative ease between the structural units composing them, inasmuch as the forces binding the units together in the direction of the *c*-axis are relatively weak. Fragments of these minerals are therefore flake-shaped, and clays may be looked upon as aggregates of flake-shaped particles. Breakage along the cleavage surface takes place more readily in the montmorillonite minerals than in the kaolinite minerals. The former minerals exist in, or can easily be broken down by working with water to, a smaller particle size than the latter. Analyses of numerous samples of illite indicate that this property is variable for members of this clay-mineral group. Some illites exist in, or can be broken down easily by working with water to, a minute particle size, whereas others exist in larger particles and are not reduced in size readily by similar working. Structural reasons for the ease of breakdown of different clay minerals will be considered presently.
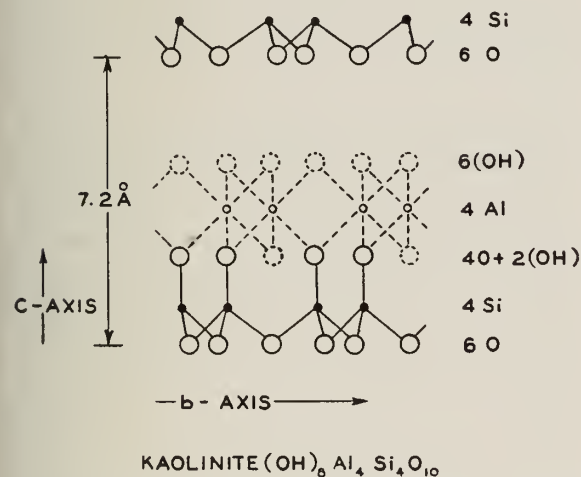

KAOLINITE $(OH)_8 Al_4 Si_4 O_{10}$

Fig. 3.—Schematic presentation of crystal structure of kaolinite (modified after Hofmann, *et al.*, *Z. Krist.*, **86** [5–6] 340–48 (1933)).

(3) Base Exchange

Clay minerals possess the property of base exchange,* *i.e.*, they may contain certain bases, which under

proper conditions are exchangeable for other bases. Different clay minerals have different exchange capacities as shown in Table I.

TABLE I
BASE-EXCHANGE CAPACITY
(me. / 100 g.)

Montmorillonite	60–100
Illite	20– 40
Kaolinite	3– 15

Recent work indicates that there is an increase in exchange capacity with decreasing particle size. The ease with which a given ion can be replaced by another is associated with the hydration of the ion and its valence. The lower the hydration and the greater the valence, the more difficult the replacement. The following order of exchangeability has been given for the common ions, $Na > K > NH_4 > Mg > Ca$. The exchange characteristics of the hydrogen ion are anomalous. The extent to which the exchange reaction proceeds depends also upon the concentration of the solution and perhaps on other factors.

IV. Relation of Structure to Base Exchange and Particle Size

Montmorillonite with the ideal composition $(OH)_4$-$Al_4Si_8O_{20}\cdot xH_2O$ is made up of units in which all the charges are balanced. There are no excess charges on the lattice to hold exchangeable bases or to hold the units together. Montmorillonite, however, has high base-exchange capacity, higher than can be accounted for entirely by broken bonds at the edge of fragments. Analyses of montmorillonites usually show some divergence from the ideal composition, particularly by their content of magnesium, indicating replacements within the lattice, and to such replacements may be assigned the cause of some of the exchange capacity and other properties.

The magnesium contained by montmorillonite probably, at least in part, exists as replacements by Mg^{++} of Al^{+++} positions in the gibbsite layer, thereby providing an excess charge on the lattice. The origin of this excess charge is in the center of a unit about 9 Å thick. At the surface of the units, such charges can be assumed to have the strength necessary to hold exchangeable bases but not the strength necessary to hold the units themselves together tightly. Water may enter between the units, causing the lattice structure to expand. It may be considered that the hydration of the exchangeable cation pushes the units apart. Hence, assuming such replacements of the Al^{+++} gibbsite positions, montmorillonite is built up of units loosely held together, and, as a consequence, it can expand and readily cleave into extremely thin flakes upon agitation in water, giving a huge surface area to a mass of the mineral. On this assumption, the flakes

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* Base exchange can be illustrated by the zeolite or permutite water softeners which make use of this phenomenon. Water is hard when it contains calcium compounds. As hard water passes through the softener, the calcium of the water is exchanged for sodium which the zeolite contains, *i.e.*, sodium goes from the zeolite to the water in exchange for lime which goes from the water to the zeolite, thereby softening the water. When the softener is no longer effective, sodium salt is run through it reversing the process and rendering it effective again.

would carry a charge on their surfaces adequate to hold exchangeable bases. The high exchange capacity and ability to break down into extremely minute flakes, which are characteristics of montmorillonite, may be accounted for in this way. Replacement of slightly less than 20% of the Al^{+++} gibbsite positions with Mg^{++} would provide a base-exchange capacity of about 100 milliequivalents per 100 grams.

Another type of replacement may occur in the montmorillonite structure, that is, Si^{++++} by Al^{+++} in the silica tetrahedral sheets. This replacement provides an excess charge originating near the surface of the 9Å units; it is stronger, therefore, at the surface of the units than the charge resulting from the other replacement. Such charges are assumed to be adequate to hold the unit layers in position so that water can not enter between them and cause expansion. In the montmorillonite minerals, this type of replacement is limited to an amount too small to prevent expansion. In illite, the replacement exists to the extent that about 15% of the Si^{++++} positions are occupied by Al^{+++}. The excess charge resulting from this replacement in illite is satisfied by potassium ions and the units are held together without the power of expanding. It may be considered that the units are held together through the potassium ions. The illite structure is generally similar to the structure of montmorillonite, except for replacement in the tetrahedral layer with the resulting potassium ions and the absence of expanding power. The potassium ions of illite are replaceable when they occur on an accessible surface. In the illite structure, there are also replacements in the gibbsite sheet, some of which may provide an excess charge available for a replaceable base. In illite, however, the unit layers do not expand and make available a huge surface area between the units for base exchange. As a consequence, exchange capacity is lower for illite than for montmorillonite. Furthermore, because the unit layers are held together tightly, illite does not tend to break down by agitation in water into as small flakes as does montmorillonite.

Replacements generally do not take place in the kaolinite structure, and other variations (Al^{+++} vacancies) appear to be balanced by changes of O and OH so that no excess charges develop on the lattice. Base-exchange capacity must, therefore, be attributed to broken bonds on the edges of fragments, and as a consequence it is small. The kaolinite structure (Fig. 3) is not of the expanding type, probably because of the attraction between oxygen and hydroxyl layers which are adjacent when kaolinite units are stacked one above the other (in montmorillonite, oxygen layers are adjacent in the structural units). As a result, the mineral does not readily break down into flakes of extremely small size.

V. Concept of the Make-Up of Clay

Clays are essentially aggregates of extremely minute flakes, possessing forces of varying intensity which tend to attract individuals to each other and hold them together. The force may be thought of as acting mainly from the flat surface of the flake because such surfaces make up a large percentage of the total surface area of the particle. Substitutions within the lattice which have been discussed are probably the primary cause of the attractive force.

On the addition of water to clay, a film of H_2O develops on the surface of the flakes, probably because of the attractive force and because of the presence of adsorbed cations, which tend to hydrate. The water film, which has been described as having high viscosity, may be considered to have several functions. It separates individual flakes, causing the force from the flakes to act through greater distances and thereby to hold the flakes together less firmly. It acts as a lubricant between the flakes. Water is a dipolar liquid, and the film between flakes is probably made up of oriented dipolar molecules with movement possible along planes of dipole ends (Fig. 4). It has been suggested that the flakes are held together more efficiently through oriented dipoles than through nonoriented molecules and that the lubricating effect is only possible in the presence of oriented dipoles.

CLAY MINERAL PARTICLE

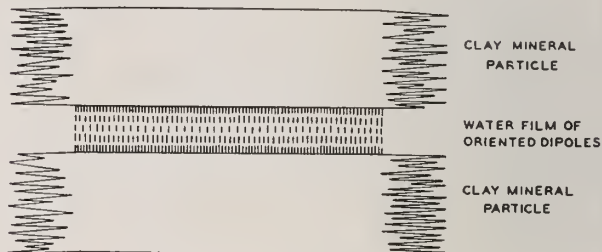WATER FILM OF ORIENTED DIPOLES

CLAY MINERAL PARTICLE

Fig. 4.—Sketch showing character of water film between clay-mineral flakes. The flakes are completely inclosed by the film. Only that part of the film directly between two flakes is shown.

On the surface of the flakes of some clay minerals, there are positions where exchangeable cations can be held. Different cations possess different hydration properties; *e.g.*, the hydration of the sodium ion is reported to be much greater than that of the calcium ion, which in turn is greater than that of the hydrogen ion. The radius of the hydration envelop around the sodium ion, therefore, is much larger than the radius of the hydration envelop around the calcium ion. The character of the cation may be considered to influence the thickness of the water film around the clay-mineral flake because of its hydration properties. A further factor controlling the thickness of the water envelop is the distance from the surface of the flake at which the cations are held, which in turn is related to their size and valence. It follows from this discussion that sodium montmorillonites would possess a tendency to build up a thicker water film than the hydrogen montmorillonites. This is in agreement with the well-known fact that sodium bentonites (composed of montmorillonite) swell markedly in water, whereas hydrogen bentonites swell little or not at all.

The unfired physical properties of clay, *i.e.*, plasticity, bonding strength, shrinkage, retention of form, etc., may be ascribed (1) to the structure and composition of the constituent clay minerals which determine the particle size on working with water and the

attractive force between particles and (2) to the character of the exchangeable bases. By composition is meant the make-up of the clay mineral, particularly in regard to substitutions within the lattice. Two montmorillonites, identical except for differences in Mg^{++} replacements of Al^{+++} gibbsite positions, may be expected to impart different physical properties to clays containing them. Properties depend not only on the presence of montmorillonite but on the composition of the particular montmorillonite in a given clay. Unfortunately, analytical procedures are not precise enough to raise above the realm of speculation many points regarding lattice substitution within the clay minerals. The water film on the surface of the clay-mineral flake results both from the structure-composition factor and the factor of exchangeable base. The phenomenon of plasticity results from the interplay of the attractive force tending to hold the clay-mineral flakes together, the thickness of water film keeping the flakes apart, and the lubricating properties of the water film. Best working properties depend on the relation of thickness of the water film to the strength of the force. A clay composed of flakes with high attractive force and thin water film (because of an exchangeable cation of low hydration ability) held close to the flake surface would, on the basis of this concept, yield a sticky plastic mass. A clay with high attractive force and thick water film, because of a highly hydrated cation held a greater distance from the flake surface, or a clay composed of a clay mineral with low attractive force would yield a plastic mass with less stickiness. It has long been recognized that the phenomenon of plasticity in all clays is not the same and, on the basis of this concept, differences can be explained.

Many investigators have related plasticity and other green properties to flake-shaped particles and their surface film of water. The present study attempts to carry this concept back into the structure of the units composing clays.

Although it is aside from the object of the paper to consider the influence of constituents other than the clay minerals on the properties of clays, it may be pointed out that angular grains of quartz, feldspar, etc., would disrupt the make-up of a clay leading to plasticity, just as grit between two lubricated steel surfaces disrupts the action of a lubricant. The well-known tendency of such material to reduce plasticity is in accord with this concept. It is well known that colloidal organic material influences the green properties of clays. The exact mechanism of the effect is not clear, but in general the action results from an effect on the water-film characteristics.

VI. Influence of Clay Minerals on Unfired Properties

(1) Montmorillonite Group

It follows from the foregoing discussion that a clay composed of montmorillonite, upon working with water, will be composed of a large number of extremely minute flakes. Charges will be present on the surface of the flakes adequate to hold exchangeable bases and to provide a certain attractive force between particles. Conditions are proper, therefore, for the development of water films on the flakes, and with the attractive force between flakes, the situation fulfills the requirements for the plastic state in clays. The great number of such flakes in a montmorillonite clay, or more properly the great number of water films between flakes along which slippage can take place, indicates that the order of plasticity of such clays will be high. The huge surface area for the development of water films also indicates that water of plasticity and drying shrinkage will be relatively high. The large total surface area possessing attractive force suggests that bonding power will also be high. Although the attractive force (because it comes from the center of the cell) is not great individually, the huge total number of such charges dictates that their mass effect will be large.

Inasmuch as montmorillonite clays have high base-exchange capacity, the unfired properties of montmorillonite clays will exhibit considerable variation, depending on the exchangeable cation present.

(2) Illite Group

Clays composed of illite are aggregates of flakes with attractive forces on their surfaces. Like clays composed of montmorillonite, conditions are proper for the development of water films surrounding the flakes and for the existence of the plastic state when the clay is worked with water. Because of the structural conditions noted previously, however, flakes of illite are larger than those of montmorillonite, and there would be fewer of them in a given volume of clay. There would then be a smaller total surface area and consequently fewer water films between flakes along which slippage could take place in an illite clay. The plasticity of such clays would, therefore, be relatively less than that of montmorillonite clays. It follows that the water of plasticity, drying shrinkage, and influence of exchangeable bases on properties would be lower in illite than in montmorillonite clays. Replacements in the tetrahedral silica sheets, which are near the surface of the structural units and take place to a greater degree in illite than in montmorillonite, may mean that the attractive force on the surface of the individual units is stronger for illite than for montmorillonite. In illite, however, the individual units are bound together into larger flakes so that the charge on many units does not influence properties. Only the attractive forces of the units making up the outsides of the flakes are important. The attractive force of inside units serves only to hold them together to make up the flake. As a result, the number of flakes in an illite clay is so much less than in a montmorillonite clay that the total attractive force in a given volume of clay would be less. Illite clays, therefore, would generally have lower bonding power than montmorillonite clays.

The amount of Al^{+++} replacing Si^{++++} in illite varies from little, when the mineral approaches montmorillonite, to much, when the mineral approaches muscovite in structure. When little Al^{+++} replaces Si^{++++}, the units are held together less securely along the *c*-axis, and the mineral upon mixing with water

breaks down into thinner and smaller flakes than when much Al^{+++} replaces Si^{++++}. There should be a wide variation, therefore, in the physical properties of illite clays, and it has been found that some illite clays have physical properties approaching those of montmorillonite clays, whereas others have little bond strength, low drying shrinkage, and properties subject to little change because of the character of the exchangeable cation. Future work probably will indicate a subdivision of the illite group with a close correlation between members of the group and their physical properties.

(3) Kaolinite Group

The kaolinite cell does not undergo replacements which develop excess charges on the lattice, and the mineral has low base-exchange capacity. The units of kaolinite are held together securely along the *c*-axis so that there is little tendency for the mineral to break down into extremely small and thin flakes in the presence of water.

Clay composed of kaolinite may be viewed as an aggregate of small flakes (not so small as those of montmorillonite or some illite clays) which are not charged. There is, therefore, slight tendency to form water films on the flakes and for the individual flakes to attract each other. As a consequence, bond strength, drying shrinkage, and general plastic properties should be low. Water of plasticity should be well below that of montmorillonite clays and subject to variation, depending on the size of the kaolinite particles. Because the base-exchange capacity is low, properties of the kaolinite clays depend little on the character of the exchangeable base.

Theoretically, it would seem that montmorillonite and some types of illite clays should have much greater plastic properties and bonding strength than kaolinite clays and other types of illite clays. This is in agreement with the well-known fact that a small amount of montmorillonite clay, *e.g.*, bentonite, added to clays of low plasticity and bond strength, greatly increases these properties. For these reasons and also because of petrographic analytical data for a wide variety of clays, the writer has reached the conclusion that the unfired properties of clays are frequently determined to a large degree by the amount of montmorillonite or illite of a certain type which they contain. For example, in china clays, which are essentially kaolinite clays, very small amounts of montmorillonite or illite may be the chief factor in determining unfired properties, the influence being out of all proportion to the abundance of these minerals. The quantity may be too small to permit detection when a bulk sample is studied. Only by fractionation of the finest grade sizes does the constituent, which may be largely responsible for the properties, become evident.

VII. Influence of Exchangeable Bases on Physical Properties

Only an incomplete discussion of this subject is possible because of the general unsatisfactory condition of the available data which are scant and frequently contradictory. Reports of the influence of electrolytes on clays are of little value unless the amounts of actual base exchange and the mineral composition are recorded. The lack of adequate tests for measuring such properties as plasticity is an added difficulty.

Primarily, the influence of various cations on many physical properties is determined by the degree of their hydration and the distance they are held from the surface of the particle, and consequently with the character and thickness of the water film developed. By character is meant particularly the perfection of orientation of the water dipoles; there is some reason to believe that the degree of orientation may vary with the cations present. Sodium ions carry much water and are loosely tied to the surface of the flake. Calcium and magnesium ions are more solidly held and carry less water than sodium ions. Hydrogen, aluminum, and iron are firmly held and carry less water than the bivalent ions. A further important factor is the disrupting influence of some cations, particularly Na^+, in clays of certain types. Highly hydrating Na^+ in montmorillonite tends to produce a spreading apart of the structural units along the *c*-axis, with a consequent breakup of the clay particle into extremely minute flakes. There is much less tendency for spreading of the structural units of a hydrogen-montmorillonite clay, so that upon working with water, a sodium-montmorillonite clay will be made up of a greater number of smaller flakes than a hydrogen-montmorillonite clay. The character of the exchangeable cation, therefore, also influences properties because of its influence on the particle-size distribution of the clay when worked with water.

Some investigators consider that Na^+ increases the plasticity of clays; others, that this property is decreased by Na^+. Cations of low hydration, such as H^+ and the trivalent ions, Al^{+++} and Fe^{+++}, impart low plasticity to clays. Recent studies indicate that the best working properties are found when an ion of intermediate or relatively low hydration, like Ca^{++}, is the exchangeable base present. Available data indicate that water of plasticity is higher for the hydrogen clays than for those carrying alkalis.

Substitution of sodium for other exchangeable bases tends to increase drying shrinkage. Clays with Al^{+++} or Fe^{+++} have lower shrinkage than those carrying Ca^{++} or Mg^{++}, and these clays in turn have less drying shrinkage than those with Na^+.

Green strength tends to be higher for hydrogen clays than for clays carrying sodium. Clays with the divalent ions possess an intermediate strength. In some utilizations of clays, it is necessary to determine a green and a dry strength in clay-sand mixtures. Hydrogen bentonites are known generally to have higher green strength than sodium bentonites, and frequently the latter have greater dry strength than the former. The explanation for this situation is by no means clear, but it would seem to be related to the difference in the disrupting ability of Na^+ and H^+, that is to say, dry strength is closely related to particle size, whereas green strength is more closely related to the thickness of the water film on the flakes.

Almost all clays with high ability to remove the color from oil are composed of members of the montmorillonite group or certain types of illite. The efficiency of many bleaching clays is increased by acid treatment. It has been suggested that decolorizing ability is related to the presence of H^+ and Al^{+++} in proper proportions as exchangeable cations.

VIII.   Influence of Clay Minerals on Fired Properties

There has been little study of this problem, and the scant available data permit only a few general conclusions. It is made difficult by the fact that the proportionate influence of minor constituents and impurities on fired properties is greater than on green properties. Thus, a trace of an impurity may seriously influence firing properties but have no effect on unfired properties.

Minerals of the illite and montmorillonite groups contain ferric iron replacing aluminum, and a red or yellow firing color results. Some exceptional clays are known to contain much illite and practically no iron. These clays, of which Valendar clay is an example, have a light-firing color. Iron does not appear as a replacement of aluminum in the kaolinite structure, and consequently kaolinite clays are light or white firing.

Minerals of the illite and montmorillonite groups contain alkalis and alkali earths either within the lattice or as adsorbed ions. Because of these constituents and because of the usual presence of iron, clays composed of these minerals are not refractory. Kaolinite contains no alkalis or alkali earths, and consequently kaolinite clays are refractory.

IX.   Particle-Size Grade Distribution

A large amount of important work has been done on the size-grade distribution of clays and on the relation of particle size to physical properties. Mechanical analyses of clays attempt to classify the constituents according to particle size, and because clays are essentially composed of clay minerals, the object is to determine the size in which the clay minerals exist. Clay-mineral studies indicate that certain characteristics of these minerals must be taken into account in making such determinations.

Analyses of clay are made using water. The determination of size is preceded by a process of dispersion to place the clay in suspension. It is obvious from the previous discussion of clay-mineral properties that dispersion of a clay in water will tend to break up the clay-mineral particles by cleavage along the basal plane and by breakage across thin flakes. The Attapulgus fuller's earth illustrates the phenomenon. A thin section study of this clay shows it to be composed largely of clay-mineral particles several microns in diameter. The clay is easily disaggregated and dispersed so that wet analysis shows almost all of the clay to be composed of particles smaller than 1 or 0.1 μ. In making mechanical analyses of clays, the measurements made clearly represent the degree of disaggregation and frequently nothing else. There may be no relation between the size-grade distribution determined and the size-grade distribution of the natural clay.

In utilizing clays with water in which there is a certain amount of working of the clay, there is also the tendency to break down the clay-mineral particles. Correlation of size-grade distribution and properties depends on the assumption that the breakdown of particles is the same order of magnitude in analysis and in working. In such correlation work, the objective should be to determine the effective particle size, *i.e.*, the particle size of the clay as it is actually used.

It is clear from the previous discussion of clay mineralogy that montmorillonite breaks down much more easily during analysis than does kaolinite. Some illites retain their size during dispersion and analysis, whereas others are easily reduced. Mechanical analyses of kaolinite clays give a fair picture of the make-up of the natural clay, whereas analyses of montmorillonite clays measure little more than the degree of disaggregation.

X.   Analytical Data for a Group of Typical Clays

Table II presents the mineral composition of a variety of clays and shales together with determinations of certain of their physical properties and textural characteristics. The relative values for ceramic properties of kaolinite, illite, and montmorillonite clays, respectively, are in agreement with those anticipated on theoretical grounds. Complete detailed correlation can not be expected unless other factors such as base-exchange characteristics are also considered.

Water of plasticity is much higher for montmorillonite clays (samples Nos. 12, 13, 14, and 15) than for those composed of illite and kaolinite. Water of plasticity tends to be higher for kaolinite than for illite clays, although some of the latter yield fairly high values (sample No. 11).

Modulus of rupture of the pure kaolinite clays (samples Nos. 1 and 2) is low, lower than that for illite. The high strengths of samples Nos. 3, 4, 5, and 6, which are also kaolinite clays, are due to the presence of constituents other than kaolinite, *e.g.*, organic material, certain kinds of illite, and montmorillonite. Shale samples Nos. 9 and 10 are illustrative of illite material with low modulus of rupture, and sample No. 11 shows an illite clay with high modulus of rupture. The high shrinkage of montmorillonite makes accurate modulus of rupture determinations impossible. The values for mixtures of 95% sand and 5% clay show the high strength of montmorillonite and some illite. Shrinkage is high for the montmorillonite clays and low for illite and kaolinite clays. The kaolinite clays appear to have higher dry shrinkage than firing shrinkage, whereas in illite clays the firing shrinkage is higher.

The data show clearly the refractory and light-firing character of kaolinite clays and the nonrefractory and dark-firing character of illite and montmorillonite clays. Clays composed of illite and montmorillonite have a tendency to bloat.

The kaolinite and illite clays contain varying but usually small amounts of material in particles easily reduced to less than 1 μ and very small amounts reducible to less than 0.1 μ. Some illite clay-mineral

TABLE II

SOME PHYSICAL PROPERTIES OF CLAYS WITH DIFFERENT MINERAL COMPOSITIONS*

Sample No.	Character of material	Water of plasticity	Modulus of rupture	Modulus of rupture with 50% sand	Green compression strength with 95% sand†	Linear drying shrinkage	Linear firing shrinkage	Firing color	P.C.E.	Per cent <0.001 mm.‡	Per cent <0.0001 mm.‡	Mineral composition§
1	N. C. washed china clay	43.8	166	82	0.8	7.3	5.6	White	32	19	1	Kaolinite, VA; quartz, R; feldspar, R; illite, VR; montmorillonite (?)
2	Ill. sedimentary kaolin	38.3	192	152	0.4	8.0	5.6	Cream-white	32	64	10	Kaolinite, VA; quartz, R; illite, VR; montmorillonite (?)
3	Ill. Cheltenham underclay	36.2	378		0.8	10.0	6.5	Buff	28	50	15	Kaolinite, VA; quartz, A; illite, R; montmorillonite (?)
4	Ill. underclay	30.0	497		0.9	6.8	5.0	Buff	27	46	13	Kaolinite, VA; illite, VC; quartz, VC; montmorillonite (?)
5	Ky. ball clay	45.7	608	457	1.0	6.6	11.0	Cream-white	32	72	35	Kaolinite, VA; illite, C; quartz, C; montmorillonite, R
6	German Valendar clay	37.0	353	183	0.8	8.9	7.4	Cream-white		85	35	Kaolinite, VA; illite, A; quartz, C; montmorillonite, R
7	Ill. Cretaceous clay	22.2	217	214	0.4	9.8	7.2	Red	31	30	8	Quartz, VA; kaolinite, A; illite, VC; montmorillonite (?)
8	Ill. Cretaceous clay	29.1	283		0.6	7.5	6.2	Gray	25	28	10	Illite, VA; quartz, VA; montmorillonite (?)
9	Ill. Pennsylvanian shale	28.8	302	183	0.8	5.9	12.0	Red	10	13	3	Illite, VA; quartz, VC; chloritic mica, R; limonite, VR
10	Ill. Pennsylvanian shale	24.0	214	133	0.6	4.8	10.0	Red	9	16	5	Illite, VA; quartz, A; chloritic mica, R; limonite, VR
11	Ill. underclay	40.1	537	268	2.8	10.9		Red	12	60	40	Illite, VA; quartz, VC; kaolinite, C
12	Ill. fuller's earth	82.9	275		2.5	13.0	20.1	Yellow-buff	12	39	17	Montmorillonite, VA; quartz, VC; glauconite, C; illite, C; kaolinite (?)
13	Ga. Attapulgus fuller's earth	92.6	649	150	2.7	15.0	23.2	Buff	12	68	59	** (?) VA; quartz, C; illite, VR; glauconite, VR
14	Ga. Pikes Peak fuller's earth	90.0	830	172	2.0	16.7		Buff	12	70	55	Montmorillonite, VA; quartz, A
15	Wyo. bentonite	114.6			3.4	18.5		Buff	12	80	70	Montmorillonite, VA; feldspar, R; quartz, VR

* Compiled from published data and data in the files of the Illinois State Geological Survey.
† Using 5% water, which is not the optimum amount for the greatest strength of all samples.
‡ Determined by method of Bray, Grim, and Kerr.
§ VA = 40%; A = 40-25%; VC = 25-15%; C = 15-10%; R = 10-5%; VR = 5%.
** The chief constituent of the Attapulgus fuller's earth has been identified by some workers as montmorillonite and by others as a mineral similar but not identical to montmorillonite.

particles are readily reduced to less than 0.1 μ; samples Nos. 5, 6, and 11 contain such illite and hence show large amounts of material in this size-range. Clays composed primarily of montmorillonite minerals (samples Nos. 13, 14, and 15) show large amounts of material of less than 1 μ and almost the same amount of less than 0.1 μ. Sample No. 12 seems to be an exception, but this clay contains much nonmontmorillonite material, has a montmorillonite with unusually high silica content, and contains free silica probably acting as a cement for the individual clay mineral particles, which may explain its exceptional grain size.

Determinations of particle size and mineral composition of many clays and shales have shown that kaolinite and most illite tend to exist in particles larger than 0.1 μ in diameter. Large particles of these minerals are not readily reduced to sizes below 0.1 μ. Montmorillonite, however, exists in particles up to several millimeters in diameter which usually can be broken down to less than 0.1 μ by simple agitation in water. This fact has been used by Bray, Grim, and Kerr as a basis for mineralogical analyses of complex clays.

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A bibliography of pertinent references from which much of the present material has been gathered is appended.

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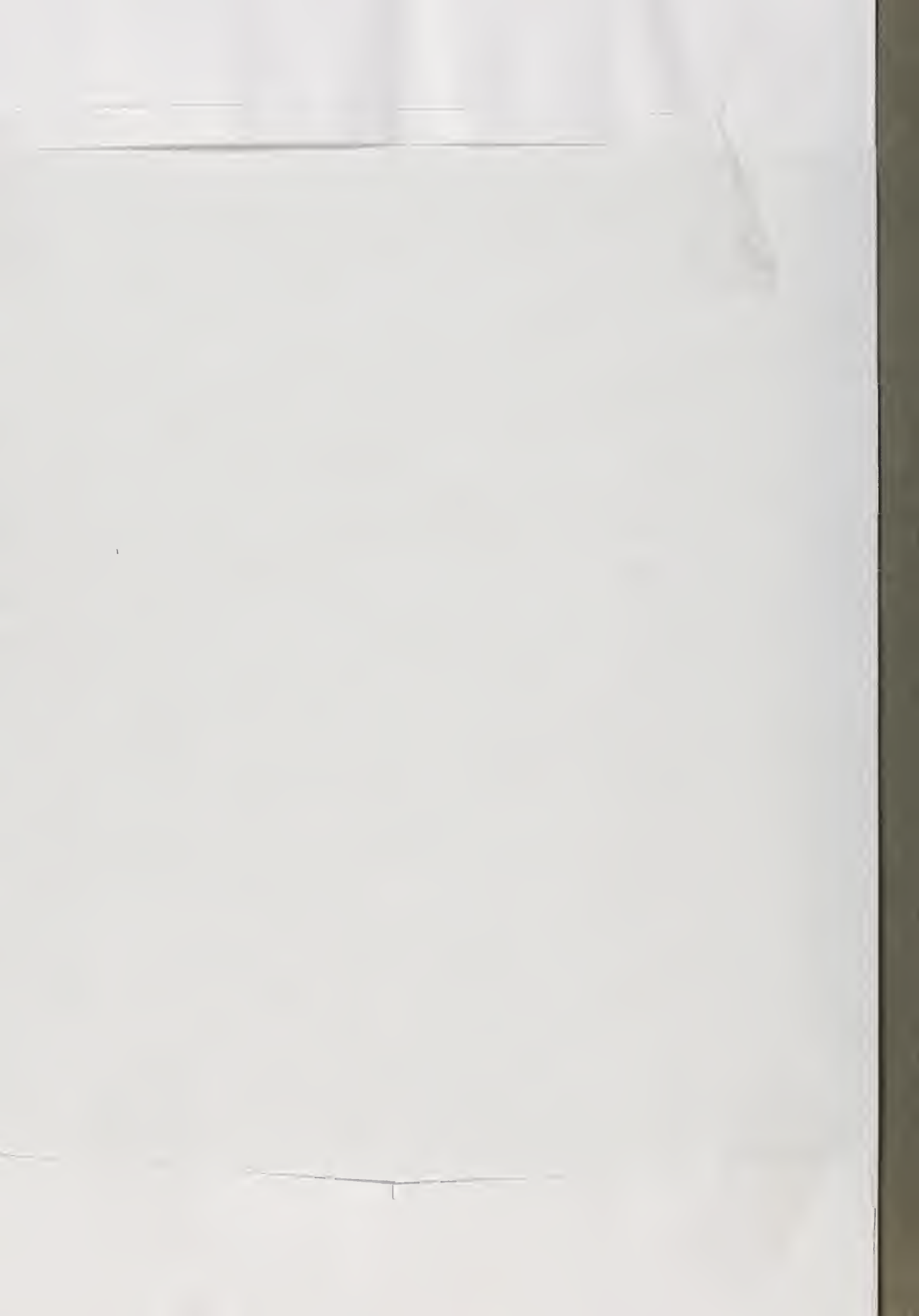
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